4051

Synthetic Organic Chemicals

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Photographic Sensitizers

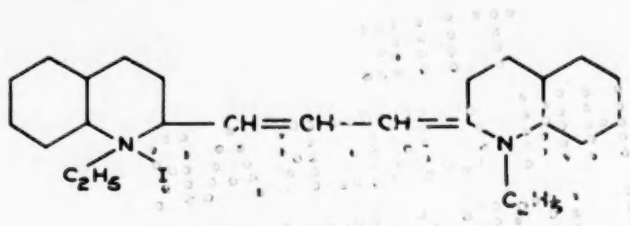
PRACTICAL photographic color-sensitizers fall into two groups, one consisting of halogenated fluoresceins (Eosin and Erythrosin), and one consisting of derivatives of pyridine, quinoline and acridine. The *Isochromatic* plates of fifty years ago, sensitized with Eosin, were the first color sensitive plates to be generally used. In 1884, Eder found that Erythrosin (tetraiodofluorescein) sensitized for green light even more strongly than Eosin; this dye is now almost exclusively used for green sensitization. In the same year, Vogel discovered that Quinoline Red rendered emulsions sensitive to the yellow and orange region of the spectrum.

Little progress followed along this line until 1902, when Miethe and Traube discovered the sensitizing power of Ethyl Red. This dye is formed by the condensation of quinaldine ethiodide with quinoline ethiodide by means of alkali, and constitutes the prototype of the class of compounds called *isocyanines*. A cyanine, known as Cyanine Blue, and prepared by condensing the isoamyl iodides of lepidine and quinoline, had previously been recognized as a sensitizer, but its use was attended with fogging and bad keeping qualities. Ethyl Red was found to be free from these disadvantages, and a series of closely related isocyanines was soon prepared by the Hoechst Dyeworks by means of which sensitization could be carried as far towards the red as $\lambda 650$. The most important of these isocyanines were Orthochrome T, Pinaverdol, and Pinachrome, prepared from 6-methyl and 6-methoxy derivatives of quinoline and quinaldine ethiodides. These dyes are sensitizers for the green and orange, a region for which Acridine Orange NO, a dye of the acridine type, is also occasionally employed. Another sensitizer for the green, Pinaflavole, was placed on the market in 1919. This appears to be the condensation-product of p-dimethylaminobenzaldehyde with alpha-picoline ethiodide.

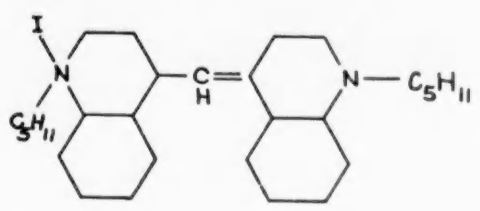
A true sensitizer for red was not available until 1906, when Homolka first prepared Pinacyanole by carrying out the Ethyl Red condensation in the presence of formaldehyde. The constitution of Pinacyanole has only recently been cleared up by the work of Mills, who has classified dyes of this type as *Carbocyanines*.

A few substituted carbocyanines have been introduced, the most valuable of these being Naphthocyanole, prepared from beta-naphthoquinaldine ethiodide. By its use photographic sensitivity can be extended to about $\lambda 750$.

Shortly after the introduction of Pinacyanole, the Hoechst Dyeworks introduced Dicyanine, a dye best produced



PINACYANOLE
(TYPICAL CARBOCYANINE)

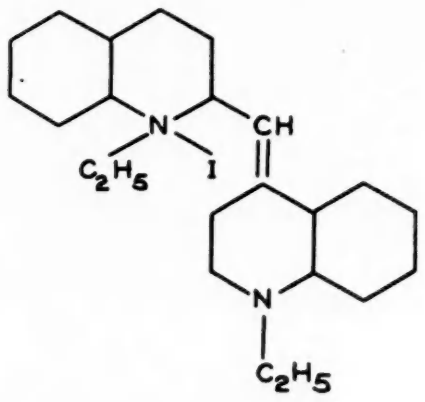


CYANINE BLUE

(as recently shown by Palkin) by the condensation of 2.4-dimethylquinoline ethiodide with chloroform by the action of sodium sulfide. The constitution of Dicyanine has yet to be cleared up satisfactorily. Dicyanine A is the analogous compound prepared from 6-ethoxy-2.4-dimethylquinoline ethiodide. By means of these Dicyanines, sensitivity can be extended to λ900, though good results are very difficult to obtain.

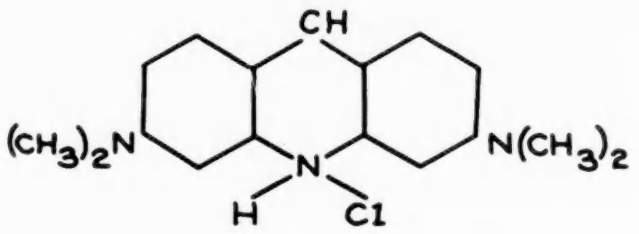
The sensitive region was extended still further by the discovery in 1919, by Adams and Haller of the Bureau of Chemistry, of Kryptocyanine. This dye is prepared from lepidine ethiodide by the method followed in the preparation of Pinacyanole from quinaldine ethiodide. Its constitution has not yet been established. It sensitizes very powerfully up to λ800, far surpassing Dicyanine for this region but at λ900 its sensitizing power is inferior to that of the latter.

In 1925, it was found in the Kodak Research Laboratories that another dye accompanies Kryptocyanine in its preparation. This, named Neocyanine, sensitizes powerfully up to λ900; and when hypersensitized with ammonia it permits



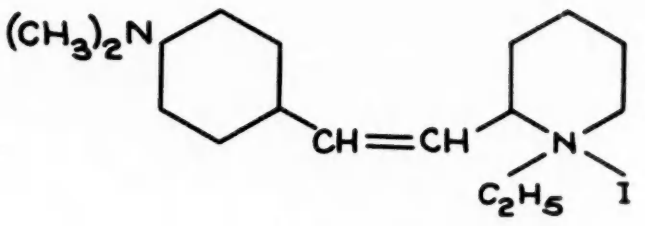
ETHYL RED
(TYPICAL ISOCYANINE)

λ1000 to be photographed with ease. In fact, with exposures of ten hours λ1129 has been reached. The constitution of Neocyanine has, like that of Kryptocyanine, yet to be elucidated.



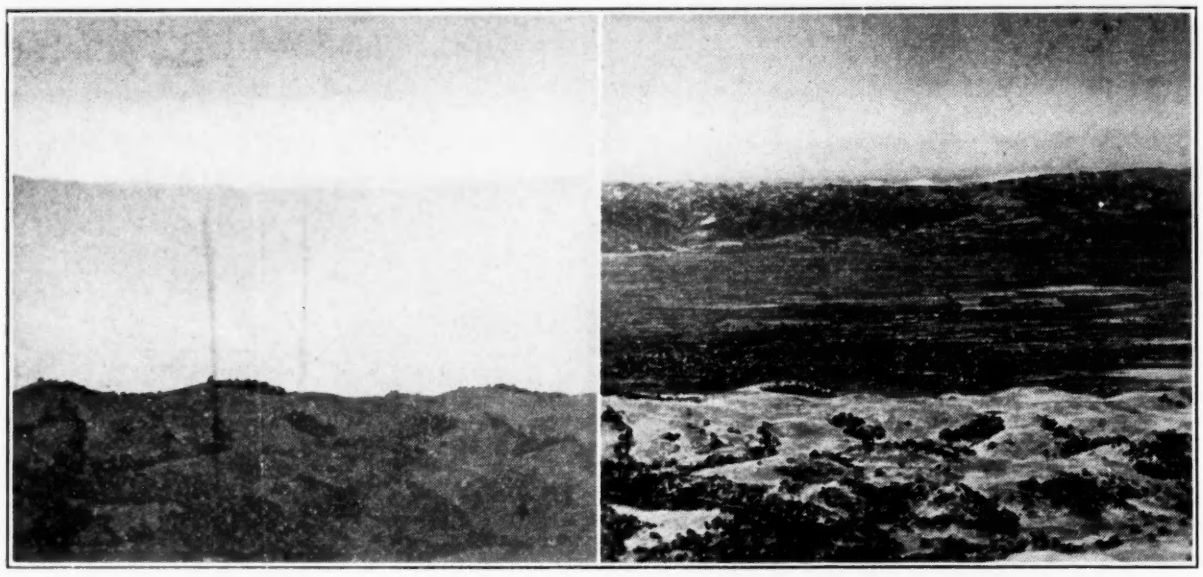
ACRIDINE ORANGE NO

These last two sensitizers are of value principally for the photography of the spectrum, and they are used largely by astronomers in their study of the stars. Kryptocyanine is used for making motion picture films in sunlight, which look as though they were taken at night, the blue sky reflecting little red light and thus appearing black. It is used also for the photography of very distant landscapes. Since atmospheric haze reflects mainly the blue and violet region of the spectrum, and the extreme red not at all, it is merely necessary to filter out



PINAFLAVOLE

the light of shorter wavelengths and photograph only the red and infra-red. In this way clear photographs can be made of scenes more than a hundred miles distant from the camera.



ORDINARY PLATE KRYPTOCYANINE PLATE

YOSEMITE VALLEY, PHOTOGRAPHED FROM MOUNT HAMILTON

These photographs of the Yosemite Valley were taken by Prof. W. H. Wright of Lick Observatory with an ordinary plate and with a Kryptocyanine sensitized plate using a red filter.

In the photograph taken with an ordinary plate, only the boundary of the hills can be seen against the sky. The Kryptocyanine plate, however, gives a perfectly clear picture through the haze, showing good detail in the hills which were one hundred and twenty miles away.

Our Plans for "Synthetic Organic Chemicals"

OUR principal object in issuing this bulletin is to keep chemists informed as to our products, and to increase the demand for synthetic organic chemicals by making their individual uses more widely known. This will include information concerning the uses of our chemicals in syntheses, in organic and inorganic analysis, in biological research, and in special work of other fields. Many organic compounds have properties of solubility or color which make them valuable in quantitative estimations, so that we plan to devote at least one column in each issue to the uses of organic reagents in analysis. This will include abstracts of general analytical methods, as well as procedures which are of value only for certain purposes or under specified conditions. The journal reference will be given in each case, and we shall be glad to furnish as much additional information as we may have on the subject.

Space will be given occasionally for laboratory "kinks," such as new apparatus or methods of manipulation which would be of interest to organic chemists. We plan to include methods which have been developed in our own laboratories or have been called to our attention by others. A list of new chemicals which have been added to our stock will be included in each issue. Many of these chemicals will be of immediate value to research workers who have had to carry out their own preparations previously.

The editorial policy as sketched above will be extremely flexible, in order that we may include from time to time, in an informal way, anything that will be of direct interest to those who work with organic chemicals. To this end we hope to have further comments and suggestions from our readers.

Organic Chemicals as Analytical Reagents

II-REAGENTS FOR COPPER (cont'd)

DINITROSORESORCINOL

Nichols and Cooper, J.A.C.S. *47*, 1268 (1925)

When 2 to 4 cc. of a saturated aqueous solution of dinitrosoresorcinol is added to a neutral solution of a copper salt, a brown precipitate or coloration is obtained depending on the amount of the metal present. This reagent may be used to determine as little as 0.004 mg. of copper in 1 cc. of solution.

HYDROQUINONE

α-NAPHTHOL

Loy and Valdiguie, Bull. Soc. Chim. *31*, 1176 (1922)

Both hydroquinone and α-naphthol give a sensitive color reaction with extremely dilute solutions of copper salts. A hot solution (0.2%) of hydroquinone barely acid with HCl, turns to an intense blue when a few drops of a dilute copper salt solution are added. When α-naphthol is used in place of the hydroquinone, a violet color is obtained. As little as two drops of a solution containing 1 part of copper in 10,000 is sufficient to give this reaction. Other metallic salts in greater concentration than 0.1% interfere with the test, so that in such cases the solution must be further diluted.

PHENOLPHTHALIN

Thomas and Carpentier, Comptes Rendus *173*, 1082 (1921)

Phenolphthalin in alkaline solution (Kastle-Meyer reagent) is oxidixed to pink phenolphthalein in the presence of minute amounts of copper. By means of this reagent, copper has been detected in distilled water where the concentration was as low as one part in one hundred million.

PYRIDINE

Spacu, Z. Anal. Chemie, *67*, 27 (1925)

Copper and mercury may be separated by means of pyridine and ammonium thiocyanate owing to the different solubilities of the metallo-organic compounds formed. The copper compound precipitates out as a fine green precipitate which may be washed, ignited to the oxide, and weighed.

BENZIDINE

TOLIDINE

Spacu, Z. Anal. Chemie *67*, 31 (1925)

If an extremely dilute solution of copper salt is treated with a few drops of an alkali thiocyanate solution and then with a few drops of an alcoholic tolidine solution, a characteristic dark blue, flocculent precipitate is formed.

Similarly, a dark blue precipitate is formed when a few drops of 1% alcoholic benzidine is shaken with a dilute, neutral copper solution, to which a few drops of potassium iodide have been added. In the absence of iron, this blue precipitate is obtained even when the concentration of copper is only 1:100,000.

ISATIN

Menke, Rec. Trav. Chim. *42*, 199 (1923)

Cuprous salts may be determined microchemically by means of a suspension of isatin in 5% ammonia. Under the microscope, this reagent shows characteristic, star-shaped crystals with cuprous salts.

New Chemicals

The following preparations have been added to our list since the last edition of this bulletin.

2.6-Dibromo-4-nitrophenol
* α.β-Dibromopropionic Acid
* *o*-Diphenylbenzene
* Ergosterol
Ethyl Fumarate
* Iodosobenzoic Acid
* Phenylethyl Cinnamate
* *m*-Toluic Acid
* Tripotassium Nitrophenoldisulfonate

* *Made or purified in the Kodak Research Laboratories.*